Polyaniline nanowires-gold nanoparticles hybrid network based chemiresistive hydrogen sulfide sensor

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We report a sensitive, selective, and fast responding room temperature chemiresistive sensor for hydrogen sulfide detection and quantification using polyaniline nanowires-gold nanoparticles hybrid network. The sensor was fabricated by facile electrochemical technique. Initially, polyaniline nanowires with a diameter of 250–320 nm bridging the gap between a pair of microfabricated gold electrodes were synthesized using templateless electrochemical polymerization using a two step galvanostatic technique. Polyaniline nanowires were then electrochemically functionalized with gold nanoparticles using cyclic voltammetry technique. These chemiresistive sensors show an excellent limit of detection (0.1 ppb), wide dynamic range (0.1–100 ppb), and very good selectivity and reproducibility. © 2009 American Institute of Physics. [DOI: 10.1063/1.3070237]

Hydrogen sulfide (H₂S) is a toxic, corrosive, and inflammable gas produced in sewage, coal mines, oil, and natural gas industries and utilized in many chemical industries. H₂S can cause blood poisoning and at high enough concentrations (higher than 250 ppm) may lead to death. Therefore, H₂S sensor that is sensitive and rapid in its response is needed.

Thick or thin film sensors based on gold and semiconductor oxides such as tin oxide, tungsten oxide, etc., have been reported.^{2,3} Doping with gold enhanced the sensitivity of the semiconductor oxide sensors.⁴ A major disadvantage of these sensors is their high operating temperatures that make them highly power inefficient and reduce their long term stability.

The promising properties of conducting polymer based materials viz (i) chemical specificities, (ii) tunable conductivities, (iii) material flexibilities, and (iv) easy processing attracted researchers to use these materials as chemiresistive sensors. 5-7 Among them, polyaniline (PANI) and polypyrrole are most frequently used and studied owing to their very good sensitivity at room temperature, good environment stability, and relative ease of processing. For gas sensing, these conducting polymers have been used primarily in the form of thin films. 8

Hydrogen sulfide is a weak acid and therefore does not interact significantly with PANI. PANI gives response to strong acid since they have the ability to fully dope PANI, which results in change in conductivity. However, a weak acid only partially dopes the PANI and does not change conductivity significantly. Although Agbor *et al.*^{10,11} reported PANI film based H₂S sensor, the sensitivity was very low. Recently, Virji *et al.*⁹ reported a proof-of-concept for chemiresistive sensing of H₂S by PANI nanofiber film composite with chloride salts of a transition metal such as cadmium, zinc, and copper. The incorporation of transition metal chlorides in PANI nanofibers improved the response to H₂S by up to four orders of magnitude compared to unmodified PANI nanofibers. The enhanced response was attributed

to the doping of PANI by HCl, a strong acid, released during the reaction of H₂S with transition metal salts. Additionally, the nanofibrous film showed better sensing performance compared to thin film because of the increased surface area.

Among the various methods that have been used to fabricate conducting polymer nanowires based nanostructure devices include the following electrochemical methods: (1) *in situ* fabrication of nanowires in e-beam lithography patterned nanochannels between a pair of electrodes, ^{12,13} (2) template directed synthesis followed by device assembly, ^{14,15} and (3) templateless synthesis. ^{16,17} Although we used the first two methods for preparing single nanowire based sensors, there are limitations in terms of device yields, scalability, and costs. Templateless synthesis of conducting polymer nanowires network is a simple and cost effective technique for fabrication of nanostructure devices based on conducting polymer and has been applied for fabrication of chemiresitive sensors. ¹⁷

In this communication we report a sensitive and selective chemiresistive sensor for H_2S detection at room temperature. The sensor consisted of PANI nanowires-gold nanoparticles hybrid network bridging a 3 μ m gap between two gold microelectrodes. A templateless two-step galvanostatic electrochemical polymerization method was applied to synthesize the 250–320 nm diameter PANI nanowires network followed by electrodeposition of gold nanoparticles.

For the synthesis of PANI nanowires network, we initially used the literature reported three continuous step galvanostatic electrochemical polymerization technique. ¹⁷ Microscopic observation of the synthesized nanostructure after each galvanostatic step revealed the formation of PANI nanowires network bridging the gap between the gold microelectrodes after two steps. Therefore, a two step continuous galvanostatic technique was applied in the present work. ¹⁸ Figure 1(a) shows the potentiogram recorded during synthesis of PANI nanowires network. The process was started by applying a constant current density of 0.08 mA/cm² for ca. ²⁰ min followed by lowering the current density to 0.02 mA/cm² for 90 min. The effective potential on the

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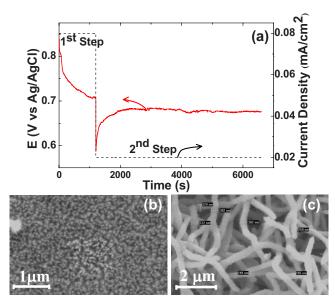


FIG. 1. (Color online) (a) Potentiogram for two-step electrodeposition of PANI nanowires, (b) SEM image of a working gold microelectrode obtained after the first deposition step, and (c) SEM image of PANI nanowires network grown on gold microelectrode at the end of second step.

working electrodes under these conditions remained at ca. 0.75 and 0.7 V (versus Ag/AgCl reference electrode), respectively. A scanning electron microscopy (SEM) image [Fig. 1(b)] of the electrodes after the first step revealed the formation of uniform PANI nuclei of ca. 50–80 nm diameter. The formation of these nuclei is essential for the growth of nanowires in the second step. ¹⁶ The SEM image of the electrode at the conclusion of the synthesis [Fig. 1(c)] indicated the nanowires network composed of numerous intercrossing PANI nanowires of diameters ranging from 250 to 320 nm. The nanowires network array fabrication technique was found to be highly reproducible.

The PANI nanowires network was functionalized with a gold nanoparticles by electrodeposition. ¹⁸ Controlled growth of gold nanoparticles of size ca. 70–120 nm was obtained by cycling the potential between +0.2 and -0.5 V (versus Ag/AgCl reference electrode) five times. Figure 2(a) shows the SEM image of gold nanoparticles functionalized PANI nanowires. The presence of gold nanoparticles was confirmed by energy dispersive x-ray analysis (EDAX) [Fig. 2(b)]. It was taken across the entire 3 μ m gap to ensure the peaks observed are from gold nanoparticles and not from gold electrodes.

Figure 3(a) shows the normalized change in resistance $[\{(R-R_0)/R_0\}$, where R and R_0 are the resistances in analyte gas and air, respectively] as a function of time of gold nanoparticles decorated PANI nanowires network and PANI nanowires network [Fig. 3(b)] to H_2S . The measurements were performed at room temperature with a 0.5 V bias potential between the source and the drain and dry air was used as the carrier gas. In accordance with the literature, there was no response as high as 500 ppm H_2S with the unfunctionalized PANI nanowires. This is attributed to the poor doping ability of H_2S because it is a weak acid. On the other hand, gold nanoparticles functionalized nanowires sensor showed an excellent response even at concentration as low as 0.1 ppb. Although the exact mechanism of the response is not known, the reaction of H_2S on the gold nanoparticles [Eq.

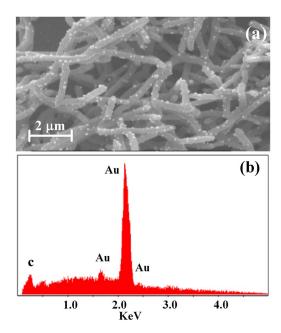


FIG. 2. (Color online) (a) SEM image of gold nanoparticles functionalized PANI nanowires network across gold microelectrodes. (b) EDAX spectrum of gold nanoparticles functionalized PANI nanowires network.

(1)] is obviously a critical step in the detection. The formation of AuS along with the enhancement of doping level of PANI from the donation of electrons to the protons released in the reaction is assumed to change the resistance of the PANI-gold nanoparticles network.³ It is also reported that PANI and gold nanoparticles act as a donor and acceptor, respectively, confirming that the transfer of electron from *p*-type PANI network increases the conductance (i.e., decreases the resistance),

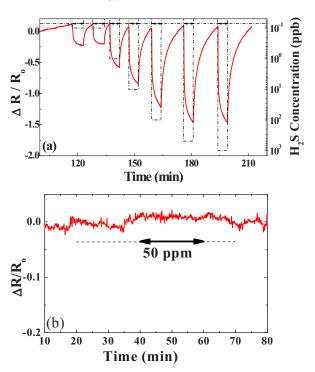


FIG. 3. (Color online) (a) Response and recovery transients (solid line) of gold nanoparticles functionalized PANI nanowire network based chemiresistive sensor toward 0.1 ppb, 1 ppb, 10 ppb, 100 ppb, 500 ppb, and 1 ppm (dashed line) concentrations of H_2S gas, (b) Response of unfunctionalized PANI nanowire network toward 50 ppm of H_2S gas (——indicates carrier gas and \longleftrightarrow indicates gas analyte).

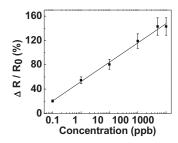


FIG. 4. Response $[\Delta R/R_0(\%)]$ of gold nanoparticles functionalized PANI nanowire network based chemiresistive sensor as a function of H_2S concentration.

$$H_2S + Au \rightarrow AuS + 2H^+$$
. (1)

The sensor had a fast response (<2 min) and recovery (<5 min) times [Fig. 3(a)] and excellent sensitivity (13.78% per ppb). The response was linear between 0.1 and 500 ppb and the inter- and intra-sensor reproducibility was good (Figs. 3 and 4). These analytical performance characteristics are superior to previously reported semiconductor oxide and conducting polymer based H₂S sensors. The sensor exhibited excellent selectivity as evidenced by only a $\Delta R/R_0$ of 5% upon exposure to 50 ppm NH₃ (data not shown), which is significantly lower than even the response to 0.1 ppb H₂S.

In summary, a conducting polymer PANI nanowiresgold nanoparticles hybrid network chemiresistive sensor for $\rm H_2S$ at ambient temperature has been described. The nanowires network of conducting polymer PANI was synthesized by a templateless two-step galvanostatic technique. Gold nanoparticles were electrodeposited on the nanowires network by cyclic voltammetry. When used in chemisresistive mode, the sensor exhibited excellent sensing response to $\rm H_2S$ in terms of limit of detection, dynamic range, response and recovery times, reproducibility, and selectivity.

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